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GCA Corp, Bedford, Mass GCA Technology Div

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Volume IV	Benzene	Volume XI	Maleic Anhydride
Volume V	Acetone	Volume XII	Dimethyl Terephthalate
Volume VI	Acrylonitrile	Volume XIII	Adipic Acid
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ASSESSMENT OF BENZENE AS A POTENTIAL AIR POLLUTION PROBLEM

Volume IV

by

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SECTION I

SUMMARY AND CONCLUSIONS

Benzene poisoning usually occurs through inhalation of the vapor, although penetration through the skin can be a contributing factor. The concentration and duration of exposure determines the severity of benzene poisoning. A concentration of 20,000 ppm is a lethal dose for man if the duration of exposure reaches 5 to 10 minutes. Acute poisoning has a narcotic effect on the central nervous system. The current OSHA standard for workers is a time weighted average of 10 ppm for an 8-hour work day and a 40-hour work week. Continual exposure to higher concentrations may cause chronic poisoning which acts through a toxic effect on the blood-forming tissues. At concentrations in the range of 5,000 to 14,000 ppm, benzene has been shown to produce acute toxic effects on plants. Benzene is only minimally reactive in photochemical smog.

Emissions of benzene occur primarily from motor vehicles, benzene production, end product manufacture, solvent usage, and storage and handling losses. Total emissions of benzene are estimated to be 1,149 million pounds per year. Vehicle emissions account for 79 percent, while benzene production, end product manufacture, solvent usage, and bulk storage account for the remainder. Estimated 1974 production of benzene was 11.6 billion pounds, and production is expected to increase at an annual rate of 7 percent for the next several years. Benzene production is concentrated in the Gulf states with 37 percent produced in Texas. However, the two largest plants producing 17 percent of the total U.S. production are in Puerto Rico. Benzene is used primarily as an intermediate in the production of ethylbenzene, phenol and cyclohexane.

Benzene emissions can be controlled by adsorption with vapor recovery or incineration. Emissions from storage tanks can be controlled through the use of floating roof tanks or fixed roof tanks vented to an adsorption or incineration unit. Although control equipment specifically for benzene emissions has not been reported in the literature, devices for the control of other similar chemicals have been reported recently. Two types of control devices are presently used in the manufacture of styrene; these are vapor recovery by adsorption and incineration. Both systems have the capability of controlling benzene, toluene and styrene emissions to almost 100 percent. Since these systems are currently being used by the styrene industry, and since benzene is closely related, it is assumed that the two control systems can also be used in the production of benzene.

Simple diffusion model calculations place the expected maximum 1-hour and 24-hour ambient concentrations in a nonwork environment at about 4 ppm and 2 ppm, respectively. These estimates apply to the largest capacity benzene production facility.

Based on the health research studies and the ambient concentration considerations presented in this report, it appears that benzene in air does not pose an imminent threat to the health of the general population, nor does it pose other adverse environmental insults as an air pollutant. However, due to the toxicity of benzene, it is concluded that a small-scale monitoring study may be appropriate.

SECTION II

AIR POLLUTION ASSESSMENT REPORT

PHYSICAL AND CHEMICAL PROPERTIES

Benzene is a clear, colorless, highly flammable liquid with a distinctive aromatic odor. Benzene can be manufactured from coal, or can be obtained from petroleum by the catalytic reforming of naphthenes or by the hydrodealkylation of toluene. It is used as a solvent and a chemical intermediate in industry, and is found in gasoline. Selected physical and chemical properties are presented in Table 1.

Table 1. SIGNIFICANT PROPERTIES OF BENZENE

Synonyms	Benzol, phenyl hydride, coal naphtha, phene, benzole, cyclohexatriene
Chemical formula	C_6H_6
Molecular weight	78.11
Boiling point	80.1°C
Melting point	5.5°C
Specific gravity	0.879 (20°/4°C)
Vapor density	2.7 (air = 1)
Vapor pressure	79 mm Hg at 20°C
Solubility	Very soluble in most organic solvents; not soluble in water
Explosive limits	1.4% to 6.8% by volume
Autoignition temperature	538°C
Flash point	-11°C (closed cup)
At 25°C and 760 mm Hg	1 ppm = 3.2 mg/m^3 1 mg/m^3 = 3.1 ppm

HEALTH AND WELFARE EFFECTS

Effects on Man

Acute Poisoning - The effect of benzene poisoning varies with the concentration in air and the duration of exposure. Flury and Zernik[1] give the following as a guide to lethal and toxic concentrations of benzene in air for a single dose to man:

Concentration	Exposure	Response
20,000 ppm	5-10 minutes	Fatal
7,500 ppm	30-60 minutes	Acute poisoning symptoms
3,000 ppm	30-60 minutes	Tolerance limit.

A concentration of 100 ppm produces only minor mucous membrane irritation.[2] Concise data are lacking in the literature on the concentration in air at which benzene begins to exert an acute effect on man. One reason for the lack of data is that individual susceptibility varies considerably. Rescuers of unconscious workmen, usually overcome in an enclosed area such as a tank containing benzene residue,[3,4,5] have died while the original victim recovered upon removal from the benzene fumes. Most industrial poisoning results from inhalation of benzene vapors. Oral ingestion causes local irritation of the mouth, throat, esophagus, and stomach, followed by blood absorption and the systemic symptoms of acute benzene poisoning. Absorption of both liquid and gaseous benzene through intact skin is poor, and is insignificant in contributing to the incidence of benzene poisoning.[6]

The data of Flury and Zernik[1] indicate that at concentrations approaching 3,000 ppm benzene has a narcotic effect on man resembling the effect of other low molecular weight compounds such as chloroform.[7] The initial exhilaration upon inhalation, greater than with chloroform, produces drowsiness, fatigue, nausea, and headache. Breathlessness, irritability,

and unsteadiness in walking may persist for 2 to 3 weeks following exposure. Higher concentrations of benzene irritate the mucous membrane of the eyes, nose, and respiratory tract. An initially high respiratory rate decreases as exposure to the vapor continues, ultimately resulting in death by circulatory or respiratory collapse.[2] Autopsy reports after acute benzene death show hemorrhage in the brain, pleurae, pericardium, urinary tract, mucous membrane, and skin. As little as 0.094 mg percent[8] to 2.0 mg percent[3] benzene by weight has been found in the blood at the time of death.

Inhaled benzene is absorbed by the body at a high rate. Humans breathing air containing 3,000 to 5,000 ppm benzene absorb approximately 80 percent of the total benzene inhaled.[9] Seventy to eighty percent benzene saturation of the blood occurs within 30 minutes.[2] Benzene has a great affinity toward specific body tissues. For example, 40 to 60 percent of the benzene in the blood can become fixed in the bone marrow, fatty tissue, and liver.[6] The fat and bone marrow especially act as reservoirs, losing absorbed benzene slowly, maintaining the poisoning effect of benzene on the body's system. Only 0.2 percent of the benzene dose is eliminated from the body as urinary benzene. Blood, fatty tissues, and bone marrow benzene is metabolized to phenol and phenol derivatives and excreted in the urine. The phenols produced by benzene oxidation are also responsible for many of the ill effects of benzene poisoning.[10] Most phenols excreted in the urine are present as detoxified conjugation products of phenol and glycine, glucuronic acid, or sulfate. When the process of conjugation is delayed, such as when there is a shortage of inorganic sulfate in the body, the phenols are left free to exert their toxic action.

Chronic Poisoning - Chronic exposure to benzene vapor over a period of years has an injurious effect on the blood forming system of the body. Numerous case studies have been reported linking a high incidence of leukemia and preleukemic symptoms in workers to benzene vapor exposure.

The symptoms have been attributed to the accumulation of benzene in the bone marrow, which is responsible for the production of red and white blood cells. A symptom of early poisoning is an increased lymphocyte count, with a total decreased white blood cell count. Later symptoms include a sharper decrease in white blood cell count, the appearance of immature and abnormal white corpuscles, and a markedly reduced white blood cell count. Up to this point, benzene poisoning can occur without any clinical signs or symptoms.[3,6] Blood tests are required to identify the poisoning. In advanced stages of poisoning, the individual will show signs of aplastic anemia: pallor, weakness, fatigue, shortness of breath, palpitation, and a progressive reduction of all blood cell types and hemoglobin. There may be bleeding of the gums and hemorrhaging under the skin due to increased capillary fragility. Different forms of leukemia can develop with or without the onset of aplastic anemia. Leukemia is generally characterized by the uncontrollable proliferation of immature white blood cells into the blood. The most common type of leukemia associated with benzene poisoning is acute leukemia characterized also by anemia, an enlarged spleen, and body hemorrhages. Bone marrow appearance can vary from that of defective development to a complete absence of development.

Table 2 summarizes studies done on individual workers relating benzene concentration to the time of exposure and the onset of disease. Table 3 summarizes the results of two studies on the effect of benzene exposure on the blood pictures of groups of workers.

Chromosome studies were performed on blood lymphocytes of workers exposed to benzene concentrations varying from 125 to 532 ppm. Significant numbers of chromosome changes were observed.[12] Similar studies were performed on persons whose bone marrow contained benzene residue, both those who had recovered from the symptoms of chronic benzene exposure, and those who had recovered from acute benzene poisoning. In both cases,

there was a persistence in stable chromosome changes – changes still present several years after benzene exposure.[13] In another example, chromosome changes were found in the bone marrow cells before the onset of leukemia. Stable chromosome changes could give rise to abnormal clones that would become leukemic.[14]

Table 2. INDIVIDUAL CASES[6,11]

Study	Age	Sex	Source	Duration	Concentration	Description
1	47	M	Shoe adhesive	14 years	210 ppm	Aplastic anemia for 2 months from acute myeloblastic leukemia
2	38	M	Roto-gravure	6 years	190-660 ppm	Death due to myeloid metaplasia of liver and spleen
3	28	M	Shoe adhesive	3 years	150-210 ppm	Death from acute myeloblastic leukemia

Table 3. GROUP STATISTICS[6]

Study	Industry	Number of workers	Concentration	Comment
1	Rubber coating	52	60-80 ppm	8-year study: 16 workers had an abnormal blood picture
2	Leatherette factory	121	78 ppm	5-year study: 80 percent had abnormal white cell function
		60	31-62 ppm	5-year study: 60 percent had abnormal white cell function
		71	24-39 ppm	5-year study: some alteration of blood elements

It can be seen from Tables 2 and 3 that chronic exposure to as little as 30 ppm benzene can upset the normal blood picture. The current OSHA standards for exposure to benzene[15] specify that a worker's exposure to benzene must not exceed a time-weighted average of 10 ppm in any 8-hour work shift of a 40-hour work week. The worker may be exposed to a concentration of benzene above 25 ppm but below a peak of 50 ppm for a maximum period of 10 minutes during an 8-hour shift.

Effects on Animals

Acute Poisoning - Rabbits have been exposed to 35,000 to 45,000 ppm benzene vapor in air[6] with the following results:

Average exposure time	Response
3.7 minutes	Light anesthesia
5.0 minutes	Excitation
36.0 minutes	Death.

Dogs exposed to benzene vapor developed hypertension, followed by paralysis of the vasomotor system due to benzene acting on the smooth muscle of the blood vessels.[2] Rats subjected to a single exposure of 18,750 ppm showed changes in the activity of enzymes in the central nervous system. However, the reaction to benzene was not the same in all neurons; varying degrees of enzymatic response were found. It was postulated that the changes in activity were due to the direct lesion of the lipoprotein membranes of the cell's structural elements by benzene or a benzene metabolite.[6]

Chronic Poisoning - Rats exposed to 1,000 ppm benzene for 23½ hours per day, 7 days per week, hemorrhaged from the nose and mouth after 183 hours; the stomach was distended and the gut was empty with a loss of body weight. The blood vessels of the lungs, liver, kidneys, intestines, and abdominal tissues were engorged. In addition, there was a low white blood cell count, an increase in the number of polymorphs relative to lymphocytes,

and a lower leukocyte DNA value. Rats exposed to 1,000 ppm benzene for only 18 hours per day had similar symptoms after 1,782 hours. Rats of this latter group showed no exposure symptoms after recovering for 6½ months except for the low leukocyte DNA value. Rats exposed for 8 hours per day, 5 days per week, to 200 ppm benzene had a fall in their white blood cell count after 750 hours. At 50 ppm with exposure for 8 hours per day, 5 days per week, up to 750 hours, there was a fall in the white blood cell count with 50 percent of the rats developing bilateral cataracts. Microscopic studies of the bone marrow in all cases showed an increase in the number of red blood cell precursors together with lower leukocyte DNA values.[16]

Benzene also acts as a central nervous system depressant. A delay was found in the conditioned reflex response time of rats exposed to benzene vapor at 20 ppm for 6 days per week, for 5½ months. No reflex delay was found at 4 ppm. It can be theorized that benzene-triggered functional disturbances of the central nervous system manifest themselves prior to the occurrence of changes in blood morphology.[6]

As in man, a typical symptom of benzene poisoning is anemia. An initial rise in blood platelets is followed by a rapid fall and anemia. There is a final fall in total leukocytes preceded by an initial rise. Benzene has been found to lower the resistance of animals to infection by reducing the number of antibodies formed, reducing the number of leukocytes, and reducing the phagocytic activity of the leukocytes. Mice treated subcutaneously with a drastic dose of benzene (1,232 mg per kg body weight) administered over a period of 52 weeks were found to contract cancer.[15]

Effects on Vegetation

Tomato, barley, and carrot plants were exposed to 7,200 ppm benzene vapor in a gas chamber.[17] Benzene had an acute toxic effect on the

plants, entering the plant tissue rapidly. A darkening of the tips of the younger leaves indicated sap leaking into intercellular spaces and tissue breakdown. As the darkening spread, there was a loss of rigidity and a marked drooping of leaves and stems. When exposed to bright light, the chlorophyll in the plants was destroyed, resulting in the complete bleaching of affected plant portions. Barley exposed to 7,200 ppm benzene vapor for 1 hour were dead within 24 hours. Tomato plants exposed for 2 hours were dead within 24 hours, while the carrots, although severely damaged, were not killed by a 2-hour exposure. Benzene was shown to be toxic only over a narrow range of concentrations. Barley exposed to 4,900 ppm benzene vapor for 4 hours were only slightly damaged 1 week after the treatment, with complete recovery 4 weeks after exposure. When exposed to 14,000 ppm benzene for 30 minutes, all the plants were dead within 24 hours.

Benzene is a contact poison in plants. Entry to the leaf is through the cuticle and stomata. When the benzene is present in sufficient concentration, the tissue dissolves due to the disruption of the lipoid elements of the cell membrane. The effect of benzene on plants is acute. Chronic toxicity has not been demonstrated, as evidenced by the recovery of some of the test plants exposed at lower concentrations.

Other Effects - Benzene and Photochemical Smog

It is well documented that the reactions taking place in photochemical smog produce ozone and peroxyacetyl nitrate (PAN), two chemical species extremely toxic to plants (and man).[18,19] Benzene is only minimally reactive in photochemical smog as compared to other aromatics such as toluene, and other hydrocarbons including most aliphatics, ketones, and aldehydes.[20,21] Photochemical reaction products involving benzene have proven capable of damaging vegetation in the laboratory,[22] but under ambient conditions and concentrations would not be significant in contributing to such damage as compared to the reaction products from the more reactive hydrocarbons.

AMBIENT CONCENTRATIONS AND MEASUREMENT

Measurements of benzene in urban atmospheres have shown concentrations to be of the order of 0.01 ppm.[23,24] A study in Los Angeles[23] revealed average concentrations of about 0.015 ppm, with a maximum value of 0.057 ppm. Concentrations measured in Toronto[24] averaged 0.013 ppm, with a maximum of 0.098 ppm.

A study[25] was conducted at typical gasoline retail service stations and bulk loading installations in Britain during the summer of 1969, mostly during warm weather and while there was a relatively high demand for gasoline. A series of 30-minute personal samples were taken at a sampling rate of 1 liter per minute during the entire work period of service station operators, and during the entire period of loading or discharging of gasoline for bulk installation operators or tank truck (road car) drivers. Nine service stations were surveyed, four of which were large and open with a high annual sales volume of gasoline, and four which were "typical filling stations" of medium size and somewhat enclosed with average annual sales. One station represented a site in dense urban areas, being very enclosed and with a relatively high annual sales volume of gasoline. Benzene content of gasolines ranged from 2.8 to 5.8 percent by volume in weather situations ranging from sunny to changeable, with variable temperature and wind conditions. Ambient benzene concentrations ranged from 0.2 to 3.2 ppm from a total of 121 tests taken. Normal handling procedures at bulk loading facilities with gasolines ranging from 0.4 to 6.8 percent benzene by volume resulted in ambient benzene concentrations ranging from 0.1 to 7.7 ppm for 70 total determinations.

Ambient Concentration Estimates

The largest installation for the production of benzene has a capacity of 160 million gallons per year. Assuming a loss of 0.5 percent, this converts to an emission rate of

$$\frac{(0.005 \text{ emission factor})(160 \times 10^6 \text{ gal/yr})(3.785 \times 10^3 \text{ cc/gal})(0.879 \text{ gm/cc})}{3.136 \times 10^7 \text{ sec/yr}}$$

= 84.4 gm/sec of benzene.

Some assumptions must be made regarding the characteristics of this benzene release to the atmosphere. In the first place, it is assumed that the concentrations of benzene are likely to be highest around production facilities. Secondly, the benzene emissions do not all come from one source, but rather from the numerous vents, condensers, valves, and reactors at the facility. Thus, the emissions can be characterized as coming from an area source which will be taken to be 100 meters on a side. Finally, the emissions do not occur at ground level, but at different heights, and an average emission height of 10 meters is chosen as a characteristic value.

Ground level concentrations can then be estimated at locations downwind of the facility.[26] To do this a virtual point source of emission is assumed upwind of the facility at a distance where the initial horizontal dispersion coefficient equals the length of a side of the area divided by 4.3. In this case:

$$\sigma_{yo} = 100 \text{ m}/4.3 = 23.3 \text{ m}.$$

Assuming neutral stability conditions (Pasquill-Gifford Stability Class D) with overcase skies and light winds, the upwind distance of the virtual point source is approximately 510 meters. With consideration of the plant boundary, it is reasonable to assume that the nearest receptor location is thus about 500 meters from the virtual point source. Finally, taking 2 m/sec as an average wind speed, the ground level concentrations may be calculated from:

$$\chi = \frac{Q}{u\pi\sigma_y\sigma_z} e^{-1/2\left(\frac{H}{\sigma_z}\right)^2}$$

or $$\chi = \frac{84.4}{(2)\ \pi\ (30)\ (18.5)} e^{-1/2\left(\frac{10}{18.5}\right)^2}$$

$$= 1.743 \times 10^{-2}\ gm/m^3.$$

for a 10-minute average concentration. Over a period of an hour this becomes (1.743×10^{-2} gm/m^3) 0.72 = 1.063×10^{-2} gm/m^3 or 3.9 ppm 1-hour average concentration. Over a 24-hour period, the average concentration might roughly be expected to about 2 ppm.

For similar conditions, the 1-hour and 24-hour average concentrations at the facility with the next greatest capacity (110 million gallons/year) would be in direct proportion to the ratio of the two capacities: 110/160 million gallons/year, or 0.69. Hence, the two time period concentrations would be 2.7 ppm and 1.4 ppm.

Measurement Techniques

Analytical methods for measuring benzene concentrations in air include ultraviolet absorption spectrophotometry, colorimetry, and gas chromatography. Air is either drawn through a bubbler or passed over silica gel or charcoal to remove the benzene sample from the air. Sensitivity, specificity, and accuracy are functions of the sampling method used and of the sampling interval. Features of the techniques are discussed below.

Ultraviolet Absorption Spectrophotometry[27,28] - Benzene absorbs ultraviolet light at a wavelength of 254.5 nanometers. Concentrations may be determined by comparing the absorbence of the sample with the absorbence

of known standards. In this technique, air is drawn through a tube containing silica gel. After collection, the silica gel is immersed in isooctane with water present. The water displaces the benzene, which in turn is dissolved in the isooctane. This method is not specific for benzene, as other aromatic hydrocarbons will interfere. The method is not sensitive enough for air pollution work, the lower detection limit being about 10 ppm of benzene.

Colorimetric Methods[27,29] - In this technique, air is drawn through a fritted bubbler containing either naphtha or alcohol, or a solution of sulfuric acid and fuming nitric acid. After preparation, the concentration in the sample is determined spectrophotometrically. The method using sulfuric and fuming nitric acid is not sensitive enough for air pollution measurements, and interferences arise from toluene, ethylbenzene, chlorobenzene, styrene, and xylene. Collection in petroleum naphtha or alcohol, however, is specific for benzene, and concentrations as low as about 1 ppm can be detected. A crimson color is produced which is read at a wavelength of 620 nanometers.

Gas Chromatography[30] - This technique is capable of detecting benzene at concentrations well below 1 ppm. Air is drawn through a tube containing charcoal on which organic vapors are adsorbed. The sample is then desorbed using carbon disulfide, and an aliquot of the desorbed sample is analyzed using a gas chromatograph. The presence and concentration of benzene are determined from its characteristic retention time and the area of the breakthrough curve.

This technique is especially well-suited for air pollution work since there is no requirement for chemicals in the field.

SOURCES OF BENZENE EMISSIONS

Benzene Production and Consumption

The production of benzene is estimated to have been 11.6 billion pounds in 1974, and it is expected to increase at 7 percent per year for the next several years.[31] Almost 45 percent of all benzene consumed domestically is used in the manufacture of ethylbenzene, which is used to make styrene. An additional 19 percent is consumed in the manufacture of phenol, an intermediate for the synthesis of polymeric materials, and 16 percent is used in the manufacture of cyclohexane. The bulk of the remainder is used in the manufacture of solvents and other nonfuel uses. A flow chart with the routes of the various benzene derivatives is shown in Figure 1, while the consumption of benzene for final products and the expected growth rate for each product are shown in Table 4.[32]

Table 4. BENZENE CONSUMPTION FOR FINAL PRODUCTS - 1974[32]

Product	Million pounds	% Annual growth
Ethylbenzene	5,140	7
Phenol	2,230	7
Cyclohexane	1,818	5
Maleic anhydride	451	13
Detergent alkylate	449	0
Aniline	412	12.5
Dichlorobenzenes	130	0
DDT	62	- 1.5
Other nonfuel uses	938	5
Total	11,630	7

Benzene is produced by 40 companies at 61 plants. Petroleum refiners and petrochemical manufacturers are the primary producers. Production

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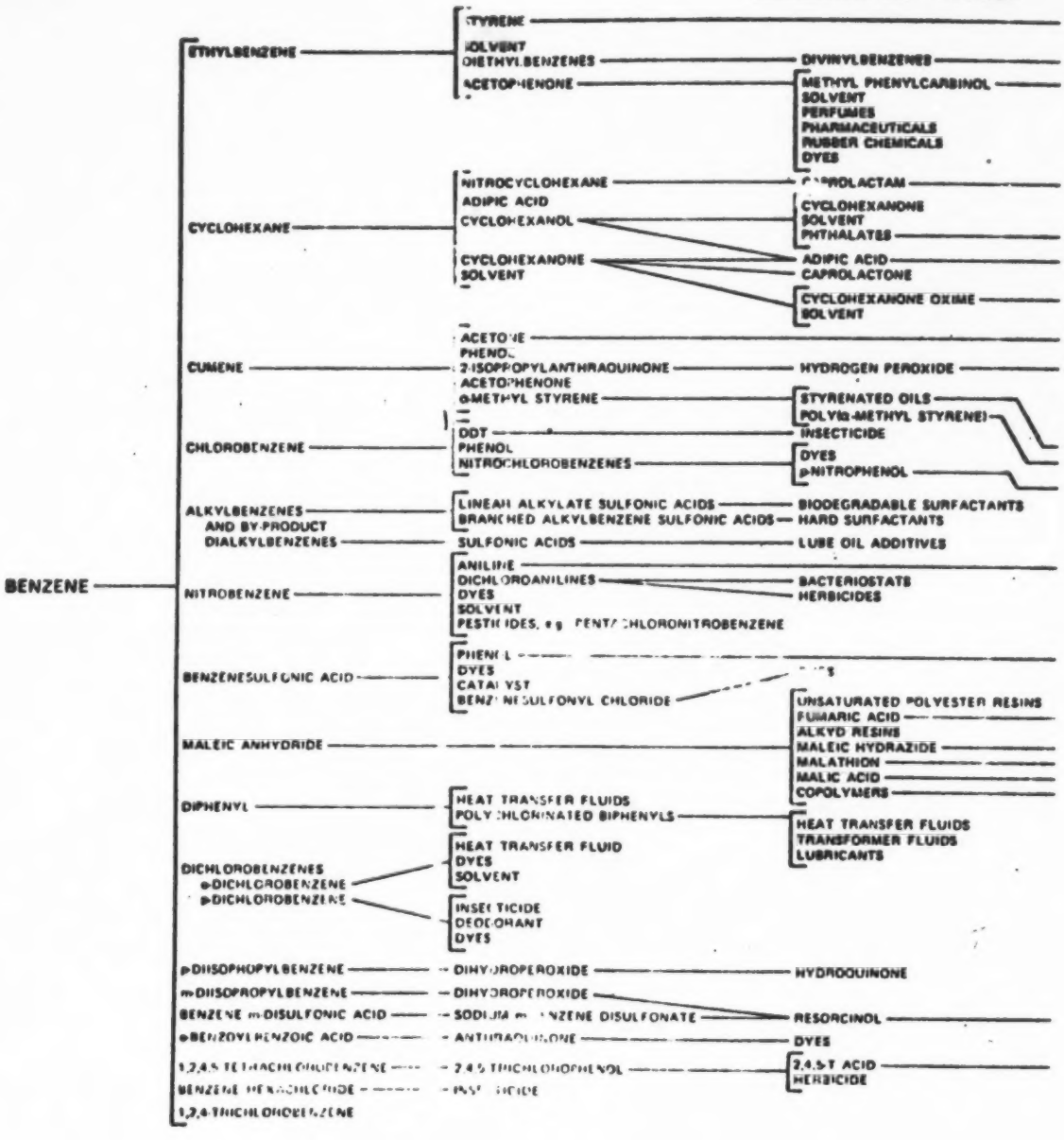

Figure 1. Benzene flow chart[33]

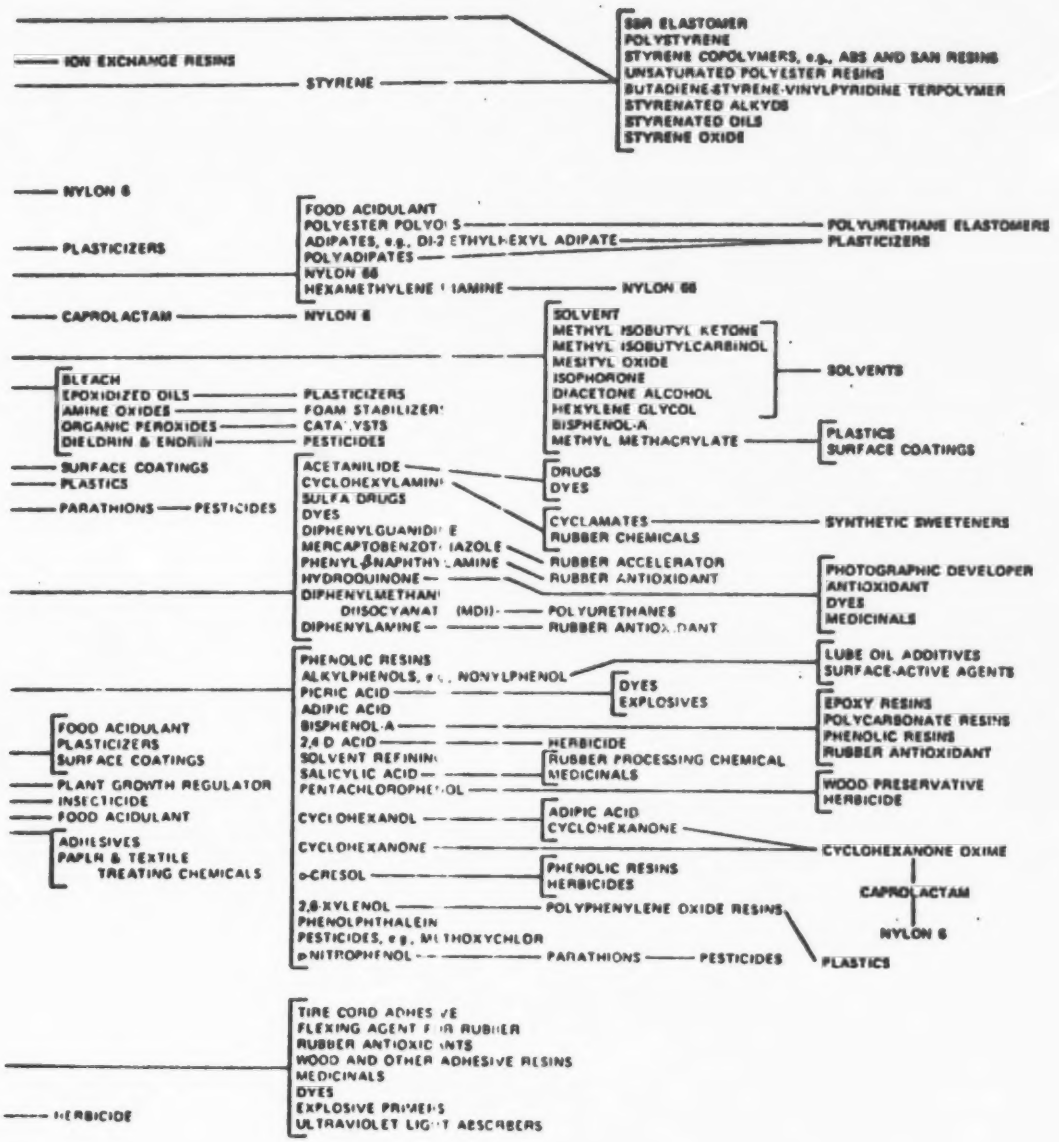

Figure 1 (continued). Benzene flow chart[33]

is concentrated in the Gulf states and Puerto Rico. The 10 largest plants account for 51 percent of total production capacity. A list of companies, plant locations, and capacity is presented in Appendix A.[33]

Benzene Sources and Emission Estimates

The major source of benzene emissions results from motor vehicle evaporative losses and exhaust emissions. Other sources of losses are from production, end product manufacturing, solvent usage, and bulk storage and handling. Total emissions of benzene (see Table 5) are estimated to be 1,148.9 million pounds.

Table 5. BENZENE EMISSIONS

Source	Million pounds
Vehicle exhaust	840.8
Vehicle evaporative loss	68.5
Benzene production	58.1
End product manufacturing	57.9
Solvent usage	54.6
Gasoline handling	35.0
Bulk storage	34.0
Total	1,148.9

Two important sources of benzene emissions, not associated with its production or its final use, are motor vehicle exhaust and motor vehicle evaporative losses. Total hydrocarbon emissions from transportation sources are estimated to have been 24,914 million pounds in 1974. This figure is calculated by extrapolating the national NEDS motor vehicle emissions from 1972 to 1974, based upon a recent transportation survey for Rhode Island.[34] This survey indicated that hydrocarbon emissions have decreased approximately 15 percent since 1972.

Approximately 75 percent of all vehicle hydrocarbon emissions result from the exhaust system.[35] Analyses of vehicle exhaust gases have indicated that approximately 4.5 percent by weight is benzene.[36] Using these two factors will result in 840.8 million pounds of benzene emitted from motor vehicle exhaust.

The remaining 25 percent of the hydrocarbon losses are a result of evaporative emissions. The concentration of benzene in gasoline varies with the type of fuel burned. A gas chromatograph analysis has indicated that regular gasoline contains approximately 1.35 percent and that premium gasoline contains approximately 0.81 percent benzene by weight. Using an average value of 1.1 percent will result in 68.5 million pounds lost to the atmosphere.

Another major source of emissions is the manufacture of benzene. Benzene is usually identified according to its source as either being coal-derived or petroleum-derived. It is currently manufactured almost exclusively (88 percent of total production) by petroleum refiners and petrochemical producers. Nine companies with 16 locations manufacture coal-derived benzene, while 31 companies with 45 locations manufacture petroleum-derived benzene.

About 70 percent of the petroleum-derived benzene is obtained from catalytic reformate, a process used primarily to manufacture high octane gasoline containing a high proportion of aromatics. Another 9 percent is a by-product of hydrodealkylating-toluene, while 11 percent is reclaimed from pyrolysis gasoline, which is a by-product of olefin manufacture. The remaining amounts are obtained when higher alkyl aromatics are dealkylated to naphthalene and from the dealkylation of toluene.

Very little data exist in the literature concerning benzene emissions. Based upon data available in AP-42[35] and emission data for other similar

processes, it is estimated that 0.5 percent of total benzene production is lost from manufacturing operations. The major sources of emissions are vents, condensers, valves, and reactors. Using the emission factor of 0.5 percent and the 1974 production rate of 11.63 billion pounds, emissions resulting from benzene production are 58.1 million pounds per year.

Similarly, it is estimated that emissions from the use of benzene to manufacture other products is also 0.5 percent. Since 11.58 billion pounds of benzene (excluding solvent usage) are used to manufacture other products, emissions from this category are 57.9 million pounds per year.

Another source of benzene emissions is its use as a solvent for paints, adhesives, and thinners. It is assumed that all benzene used as a solvent will be emitted to the atmosphere. Emissions in 1974 are, therefore, estimated to have been 54.6 million pounds.

Emissions will also occur from bulk storage and handling. Using the emission factors presented in AP-42,[35] the yearly consumption of benzene, and assuming that all storage tanks are fixed roof,[37] storage emissions are 34 million pounds per year.

The final major emission source is the distribution and handling of gasoline. In 1974, 98.1 billion gallons of gasoline were sold in the United States. Losses result from service stations and from tank truck loading and unloading. Using the AP-42 emission factors and assuming benzene is 1 percent of the vapor, 35 million pounds of benzene is 1 percent of the vapor, 35 million pounds of benzene were lost to the atmosphere from the handling of gasoline.

BENZENE EMISSION CONTROL METHODS

Benzene emissions can be controlled by adsorption with vapor recovery or incineration. Emissions from storage tanks can be controlled through the use of floating roof tanks or fixed roof tanks vented to an adsorption or incineration unit.

Although control equipment specifically for benzene emissions has not been reported in the literature, devices for the control of other similar chemicals have been reported recently.[38] Two types of control devices are presently used in the manufacture of styrene: vapor recovery and incineration. Both systems have the capability of controlling benzene, toluene, and styrene emissions to approximately 100 percent. Since these systems are currently being used by the styrene industry and since benzene is closely related, it is assumed that the two control systems can also be used in the production of benzene.

Adsorption

Control of hydrocarbon emissions by adsorption on activated charcoal is generally applied when recovery of adsorbed material is economically desirable. Adsorption should be used when concentrations of hydrocarbons are greater than 2,500 ppm. Other applications include the control of very low concentration hydrocarbons that are poisonous to catalytic incinerators and collection and concentration of emissions for subsequent disposal by incineration. Cost data for three cases utilizing adsorption are presented in Tables 6 and 7. The three cases are adsorption with solvent recovery, adsorption with incineration and no heat recovery, and adsorption with incineration plus heat recovery.

Table 6. ESTIMATED INSTALLED COSTS OF ADSORPTION SYSTEMS[a]

Adsorber capacity, SCFM	1,000	10,000	20,000
With solvent recovery, $	74,000	162,300	280,000
With thermal incineration/ no heat recovery, $	89,500	202,000	344,000
With thermal incineration/ heat recovery, $	101,500	25,500	431,000

[a]Reference 39. Inlet concentration assumed to be 25 percent of lower explosive limit. Costs updated to first quarter 1975.

Table 7. ESTIMATED ANNUAL OPERATING COSTS OF ADSORPTION SYSTEMS[a]

Adsorber capacity, SCFM	1,000	10,000	20,000
With solvent recovery, $/yr	13,200	-10,479[b]	-37,200[b]
With thermal incineration/ no heat recovery, $/yr	23,400	64,300	123,200
With thermal incineration/ primary heat recovery, $/yr	25,600	82,000	141,600

[a]Reference 39. Inlet concentration assumed to be 25 percent of lower explosive limit. Costs updated to first quarter 1975.

[b]Indicates a savings as opposed to operating cost.

Incineration

Control of benzene emissions by incineration or catalytic oxidation involves direct oxidation of the combustible portion of the effluent, the desired ultimate products being water and carbon dioxide.

The primary advantage of catalytic incineration is that extremely dilute concentrations of organics can be oxidized with only small amounts of supplemental fuel required. The one main disadvantage is that certain

hydrocarbons may poison the catalyst. Cost data for thermal and catalytic incinerators with and without heat recovery are presented in Tables 8 and 9.

Storage Tanks

Control of emissions from storage tanks would require the use of floating roof tanks or venting the emissions to the previously mentioned adsorber or incinerator. Emissions from fixed roof tanks can be vented to either system without any major increase in cost. If these systems are not available, the fixed roof tanks should be converted to floating roof tanks, resulting in a 70 percent reduction of emissions. Figure 2 provides estimated costs of various gasoline storage tanks.[39] These equipment cost estimates can also be applied to benzene. As can be seen, conversion of fixed roof tanks by installation of internal floating covers is much more economical than the installation of new floating roof tanks.

Table 8. ESTIMATED INSTALLED COSTS OF THERMAL AND CATALYTIC INCINERATORS[a]

Incinerator capacity, SCFM	1,000	10,000	20,000
Installed costs, $			
Catalytic without heat recovery	43,500	272,000	504,600
Catalytic with primary heat recovery	54,100	306,000	573,900
Catalytic with primary and secondary heat recovery	68,300	361,800	666,400
Thermal without heat recovery	27,200	92,500	137,400
Thermal with primary heat recovery	40,300	144,200	232,600
Thermal with primary and secondary heat recovery	54,400	200,000	322,300

[a]Reference 39. Inlet concentration assumed to be 25 percent of lower explosive limit. Costs updated to first quarter 1975.

Table 9. ESTIMATED ANNUAL OPERATING COSTS OF THERMAL AND CATALYTIC INCINERATORS[a]

Incinerator capacity, SCFM	1,000	10,000	20,000
Operating costs, $/yr			
Catalytic without heat recovery	16,200	102,800	195,000
Catalytic with primary heat recovery	16,400	78,500	177,900
Catalytic with primary and secondary heat recovery	19,300	108,700	203,700
Thermal without heat recovery	12,000	54,300	96,700
Thermal with primary heat recovery	11,500	36,300	59,200
Thermal with primary and secondary heat recovery	14,400	50,800	84,500

[a]Reference 39. Inlet concentration assumed to be 25 percent of lower explosive limit. Costs updated to first quarter 1975.

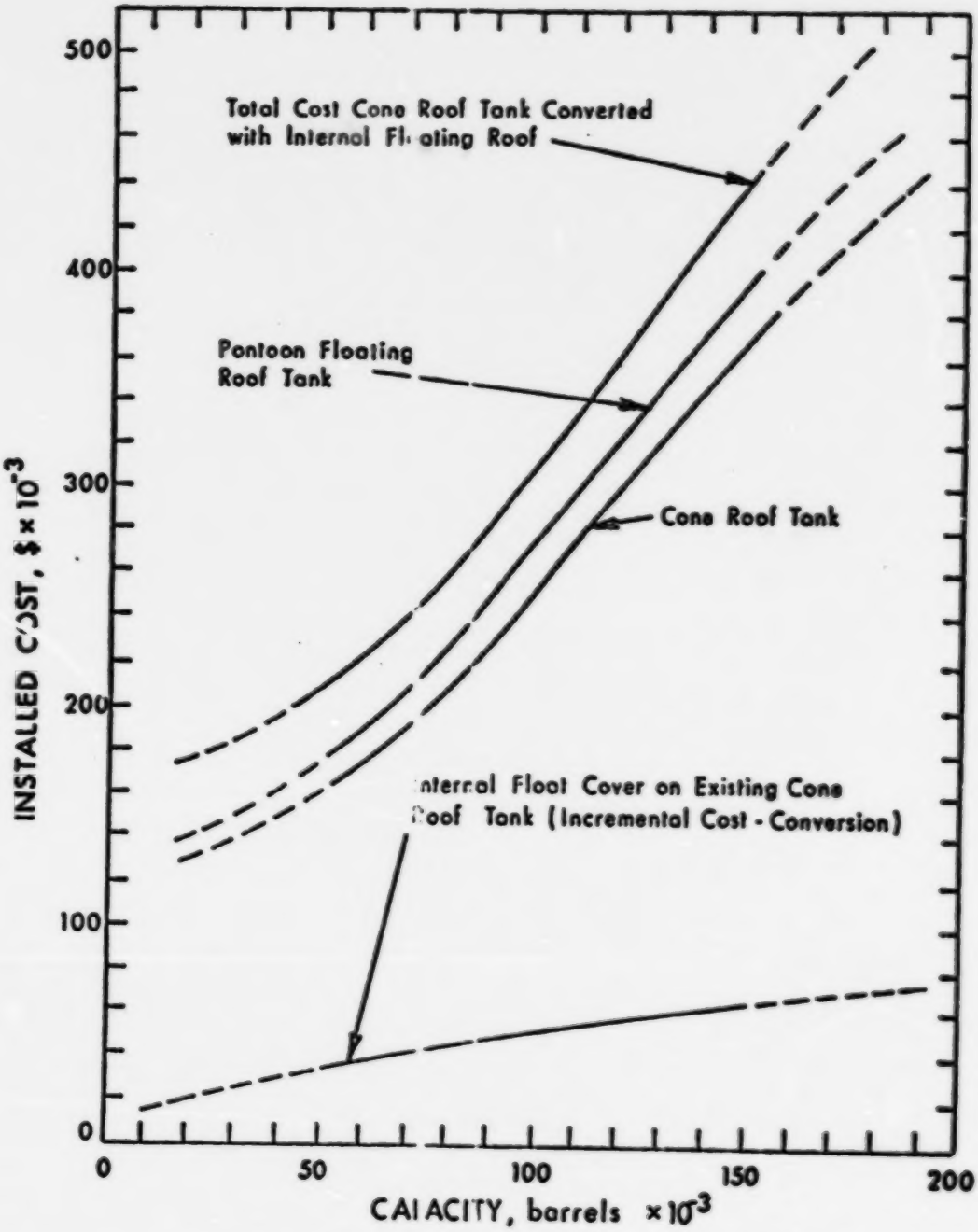

Figure 2. Estimated installed cost of benzene storage tanks (equipment costs assumed to be the same as gasoline storage tanks)[39]

SECTION III

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APPENDIX A

BENZENE PRODUCTION CAPACITY[33]

		Capacity, million gal/yr*
Coal-derived benzene		
Armco Steel	Middletown, Ohio	2.5
	Houston, Texas	0.9
Bethlehem Steel	Bethlehem, Penn.	5.7
	Lackawanna, N. Y.	7.5
	Sparrows Point, Md.	15.0
CF&I Steel	Pueblo, Colorado	3.0
Interlake	Toledo, Ohio	1.8
Ling-Temco-Vought	Aliquippa, Penn.	10.0
Mead Corporation	Chattanooga, Tenn.	0.2
	Woodward, Alabama	1.4
Northwest Industries	Lone Star, Texas	1.4
Republic Steel	Cleveland, Ohio	6.6
	Gadsden, Alabama	1.2
	Youngstown, Ohio	3.6
U. S. Steel	Clairton, Penn.	40.1
	Geneva, Utah	4.0
Total (coal-derived)		104.9

*As of January 1, 1972.

BENZENE PRODUCTION CAPACITY[33] (continued)

		Capacity, million gal/yr*
Petroleum-derived benzen		
Allied Chemical Corp.	Union Texas Petroleum Division, Winnie, Texas	5
Amerada Hess Corp.	St. Croix, Virgin Islands	23
American Petrofina, Inc.	Big Spring, Texas	30
Ashland Oil, Inc.	Ashland (Catlettsburg), Kentucky	60
	Tonawanda (Buffalo), New York	25
Atlantic Richfield Company	Houston, Texas	44
	Wilmington, California	16
Atlantic Richfield Company/ Union Oil	Nederland, Texas	18
Charter International Oil Company	Houston, Texas	8
Cities Service Company, Incorporated	Lake Charles, Louisiana	25
Coastal States Gas Producing Company	Corpus Christi, Texas	10
Commonwealth Oil Refining Company	Penuelas, Puerto Rico	160
Crown Central Petroleum Corporation	Houston, Texas	5
The Dow Chemical Company	Bay City, Michigan	30
	Freeport, Texas	40
Gulf Oil Corporation	Alliance, Louisiana	70
	Philadelphia, Penn.	33
	Port Arthur, Texas	38

*As of January 1, 1972.

BENZENE PRODUCTION CAPACITY[33] (continued)

		Capacity, million gal/yr*
Petroleum-derived benzene		
Marathon Oil Company	Detroit, Michigan	6
	Texas City, Texas	6
Mobile Oil Corporation	Beaumont, Texas	60
Monsanto Company	Alvin (Chocolate Bayou), Texas	75
Pennzoil United, Inc.	Shreveport, Louisiana	12
Phillips Petroleum Company	Sweeny, Texas	22
	Guayama, Puerto Rico	110
Shell Oil Company	Deer Park, Texas	65
	Odessa, Texas	5
	Wilmington, California	20
	Wood River, Illinois	40
Skelly Oil Company	El Dorado, Kansas	12
Southwestern Oil & Refining Company	Corpus Christi, Texas	8
Standard Oil Company of California	El Segundo, California	15
Standard Oil Company (Indiana)	Texas City, Texas	85
Standard Oil Company (New Jersey)	Baton Rouge, Louisiana	60
	Baytown, Texas	60
The Standard Oil Company (Ohio)	Port Arthur, Texas	15
Sun Oil Company	Marcus Hook, Penn.	15
	Corpus Christi, Texas	15
	Tulsa, Oklahoma	12

*As of January 1, 1972

BENZENE PRODUCTION CAPACITY[33] (continued)

		Capacity, million gal/yr*
Petroleum-derived benzene		
Tenneco Inc.	Chalmette, Louisiana	15
Texaco Inc.	Port Arthur, Texas	45
	Westville, New Jersey	35
Union Carbide Corporation	Taft, Louisiana	50
Union Oil Company of California	Lemont, Illinois	30
Union Pacific Corporation	Corpus Christi, Texas	9
Total (petroleum-derived)		1542.0
Grand total (coal- and petroleum-derived benzene)		1646.9

*As of January 1, 1972.